AD-A170 493 LASER SPECTROSCOPY OF TRANSIENT MOLECULES IMPORTANT IN EXPLOSIONS(U) ARIZONA UNIV TUCSON DEPT OF CHEMISTRY P F BERNATH 20 MAR 86 N00014-84-K-0012 1/1

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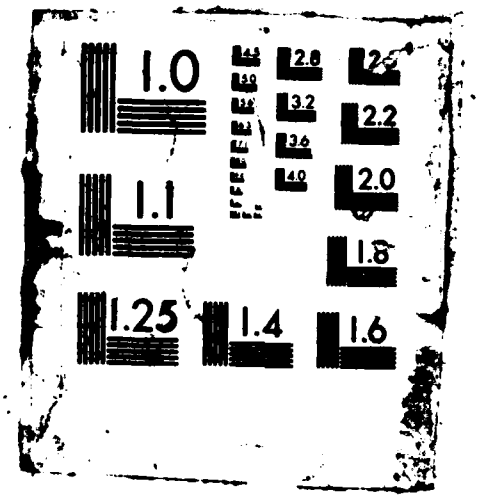
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Peter F. Bernath

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16. SUPPLEMENTARY NOTATION

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18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
explosives, detonations, Free radicals, Fourier transform spectroscopy, Laser-induced fluorescence

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Work on the spectra of the radicals NH, CCN, PH and CP is complete and in press. The vibration-rotation spectrum of CH was analyzed. The ultra-cold emission spectrum from the jet-cooled CH_3N and CD_3N radical was recorded and analyzed. The first gas-phase metal azides CaNNN and SrNNN were discovered. (keywords!)

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A. The Free Radicals: NH, CCN, CP and PH.

The spectra of these free radicals were described in previous reports. The work on these species is complete and published or in press.[1-5]

A-1

B. The Vibration-Rotation Spectrum of CH.

The CH radical is one of the most prominent and important molecules in detonations and all varieties of energetic environments. In spite of the frequent observation of the spectra of CH in many regions of the electromagnetic spectrum (microwave to ultraviolet), the excited vibrational levels of the ground state are essentially uncharacterized with the exception of v=1. Since these excited vibrational levels will be populated in energetic environments, it is important to detect them spectroscopically. The vibration-rotation emission spectrum of the $X^2\Pi$ state of CH was observed with the McMath Fourier transform spectrometer at Kitt Peak. The 1-0, 2-1 and 3-2 bands were detected in a microwave discharge of allene in Ar and methane in He. A simultaneous fit of all of the line positions provided spectroscopic constants for v=0, 1, 2 and 3. Equilibrium molecular constants (in cm^{-1}) include ω_e = 2860.4118(98), $\omega_e x_e$ = 64.1082(46), $\omega_e y_e$ = 0.2406(10), B_e = 14.45862(48), α_e = 0.53416(58), γ_e = 0.00198(15), r_e = 1.11983(2)Å. An RKR potential curve was calculated from the equilibrium constants.

C. Methylnitrene: CH_3 and CD_3N

Metal and organic ayides are widely used energetic materials. The primary decomposition products of organic azides are nitrene free radicals R-N.

The CH_3N and CD_3N radicals were made in a free radical jet source of the Engelking type. A corona-excited plasma produced from methyl azide (CH_3N_3 or CD_3N_3) in He was expanded into vacuum to provide ultracold (15K) CH_3N and CD_3N. The low rotational temperature simplifies the spectrum and allows a rotational analysis.

The CH_3N radical is closely related to NH so there is an ultraviolet $\tilde{A}^3E$-$\tilde{X}^3A_2$ transition analogous to the $A^3\Pi$-$X^3\Sigma^-$ transition of NH. The ultraviolet emission from the cold plasma was detected with the Fourier Transform spectrometer. The laser excitation spectrum was also recorded with a frequency-doubled c.w. ring dye laser. Preliminary analysis of $\tilde{A}$-$\tilde{X}$ spectrum of CH_3N and CD_3N gives an r_o structure of r_{C-N} = 1.411Å, r_{C-H} = 1.09Å (assumed) and θ_{CH_2} = 106° for the ground state. The C-N bond length is somewhat shorter (0.03-0.09 Å) than the values predicted by three recent quantum chemical calculations.

D. New Organometallic Free Radicals: CaNNN and SrNNN

We have continued work on the alkaline earth-containing free radicals such as MOR, MNCO and MC_5H_5 (M = Ca, Sr; R = CH_3, CH_2CH_3, etc.) that we have discovered with partial ONR support. The first spectrum of a gas-phase metal azide was recorded by the reaction of Ca (or Sr) with HN_3 to produce

CaNNN (or SrNNN). Metal azides are widely used in detonators.

A high-resolution analysis of the $\tilde{A}^2\Pi$-$\tilde{X}^2\Sigma^+$ transition of SrNNN established a linear geometry with a Ca-N bond length of 2.25 Å. The Sr-N vibrational frequency is 316 cm^{-1}.

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3. C. R. Brazier, L. C. O'Brien and P. F. Bernath, Fourier Transform Detection of Laser-Induced Fluorescence from the CCN Free Radical, J. Chem. Phys., in press.
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11. C. R. Brazier and P. F. Bernath, Laser Spectroscopy of Calcium and Strontium Monoazides, in preparation.

STATUS REPORT

for period

Jan 1, 1986 - Dec 31, 1986

for Contract N00014-84-K-0122

LASER SPECTROSCOPY OF TRANSIENT MOLECULES IMPORTANT IN EXPLOSIONS

A. Graduate Students

1. L. Ellinboe (O'Brien)
2. D. Bopegedera
3. S. Pianalto

B. Post-Doctorals

1. C. Brazier
2. R. Ram
3. P. Carrick (visitor)

C. Current Grant Support

National Science Foundation, 1986 - 1989, $280,000

Petroleum Research Fund, 1985 - 1988, $52,500

D. Financial Status

All funds were expended by December 31, 1986.

E. Permanent Equipment

None acquired.

STATUS REPORT

A. Personnel

Peter Bernath, P. I., Assistant Professor, summer support

Chris Brazier, postdoctoral research associate, half-time support

Ram Ram, postdoctoral research associate, half-time support

Susan Kinsey-Nielsen, graduate student (M. Sc. degree this year)

Leah Ellingboe, graduate student

Darshi Bopegedera, graduate student

B. Current Grant Support

National Science Foundation, 1983-1986, $180,000

Petroleum Reseach Fund, 1985-1988, $52,500

C. Financial Status

All funds will be expended by December 31, 1985.

D. Permanent Equipment

Ultraviolet capability (doubling crystals) for Coherent 699-29 dye laser, $10,010.

END

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